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In Search of the Molecular Triplet of C₆₀ using Low Temperature Raman Spectroscopy.

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ABSTRACT

The excited state properties of C₆₀ thin films have been probed in the temperature range 77-273K using Raman spectroscopy. The change in the Raman, 2A_g mode of C₆₀ (whose position is largely independent of temperature) was monitored as a function of the excitation intensity at 514.5nm. This mode normally positioned at 1469cm⁻¹, was seen to shift reversibly to a lower Raman frequency with increasing laser intensity. Two excited state species have been identified. The first, at 1466cm⁻¹ has been associated with the molecular triplet of C₆₀. The second species at 1463cm⁻¹, has been speculated to be an excited state co-operative involving two or more excited states in the solid and is seen to be intrinsic to solid state C₆₀ below the phase transition.

INTRODUCTION

A considerable understanding of the photophysical and photochemical properties of C₆₀ both in solution and solid has evolved over the past decade [1]. However there remains a number of important questions regarding the nature of the excited states in the solid. In solution, optical excitation leads to a population of the long lived triplet state, via the singlet state. The process has been well characterised by transient absorption measurement [2] and a strong triplet-triplet absorption at 750nm is observed [3]. However this strong feature is not observed in the solid and indeed the excited state photodynamics differ considerably from those in solution [4] leading to questions as to whether the molecular triplet exists in the solid. Further to transient absorption measurements the Raman spectroscopic signature of the molecular triplet in solution has recently been associated with a positioning of the 2A_g mode at 1466cm⁻¹ at room temperature [5]. Similar measurements however at room temperature in the solid are hampered by the much documented photopolymerisation of C₆₀ [6] which occurs via a 2+2 cycloaddition. In this paper it is proposed that below this phase transition temperature, it should be possible to isolate the intermediate excited state species associated with the photopolymerisation and thereby identify the Raman signature of the molecular triplet of C₆₀ and any differences, which exist between the excited states of isolated molecule and solid state. A temperature dependent study of the excited states will also be used to help elucidation the nature of the excited states in the solid.

EXPERIMENTAL

Gold grade C₆₀ soot obtained from Hoechst was vacuum sublimed at a pressure of 10⁻⁶ mbar onto glass substrates using an Edwards A305 coating system. The average thickness of the resulting films was ~0.8µm. Raman measurements were taken using an Instruments S.A.

Labram 1B spectroscopic microscope (x10 objective, spot radius $\sim 10\mu\text{m}$) equipped with an external Argon ion laser (514.5nm) and a Linkam microscope cooling stage. The films were allowed to equilibrate for fifteen minutes at each temperature prior to illumination.

RESULTS AND DISCUSSION

The Raman spectrum of C_{60} at 77K was monitored at laser powers of $\sim 300\text{Wcm}^{-2}$. The observed spectra were consistent with the low temperature spectra observed in previous studies where the 2A_g was seen to be independent of temperature and is positioned at 1469cm^{-1} [1, 6]. The frequency position of this mode was also found to be stable under prolonged low level illumination indicating that at the low temperature and low intensity no photochemistry was taking place. For the purpose of comparisons with earlier studies, this study will concentrate solely on the A_{2g} pentagonal pinch mode at 1469cm^{-1} [5,7,8].

Initially the laser was focused on to a single spot on the film. The incident power was then increased and the positioning of the 2A_g mode was seen to shift reversibly. In order to correlate the observed shifts with the known photodynamics of C_{60} both in solution and solid the intensity dependent transmission of the C_{60} film was monitored. In general molecular C_{60} exhibits an inverse saturable absorption due to the strong absorption of the excited state triplet in the wavelength range 650 – 790nm [2]. Figure 1(A) shows the curve obtained for the intensity dependent transmission of the C_{60} film obtained under similar conditions as the previously reported solution measurements.

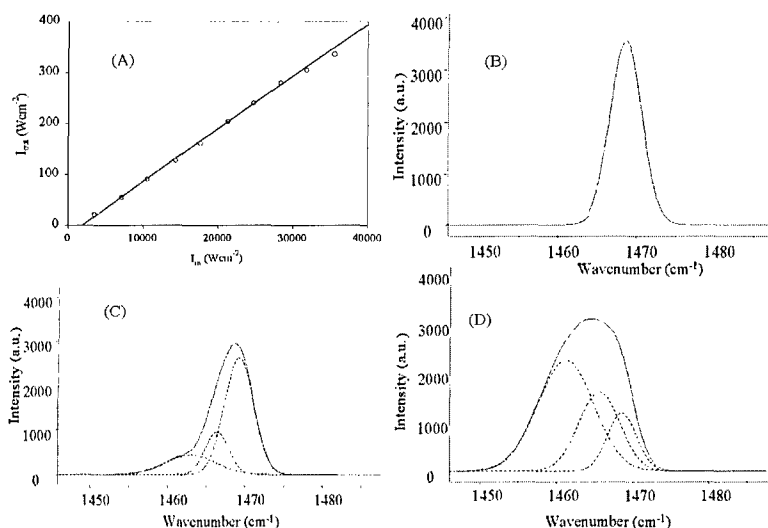


Figure 1. (A) Intensity dependent transmission curve at 77K for C_{60} film, (B), (C) and (D) are in situ Raman spectra at intensity of $\sim 3000\text{Wcm}^{-2}$, $\sim 15000\text{Wcm}^{-2}$ and $\sim 35000\text{Wcm}^{-2}$ respectively.

It can be seen that the film does not exhibit an inverse saturable absorption but rather a linear curve in the range studied. The absence of a nonlinearity does not however indicate that no population redistribution is occurring in situations where the ground state absorption co-efficient (σ_{gr}) and the excited state absorption co-efficient (σ_{ex}) are approximately equal at the wavelength employed. This may indeed be the case for C_{60} films as the photoinduced absorption spectrum for C_{60} shows that 514.5nm is situated close to the 'cross-over' or null point of the spectrum [4]. The solid line of figure 1(A) is a fit of the intensity dependent transmission given by equation 1 with a value of $\sim 2.5 \times 10^{-18} \text{cm}^2$ for the ground state absorption cross-section (σ) and $2.6 \times 10^{-18} \text{cm}^2$ for the excited state absorption cross-section (σ_{ex}) [6]. The fit yields an excited state lifetime of 7 μsec for solid state C_{60} which is comparable to previously reported life times of C_{60} [6]. Although the intensity dependent transmission is linear, it has been previously shown that a considerable excited state population can be readily produced at the intensities used i.e. at an intensity of $\sim 20000 \text{Wcm}^{-2}$ the excited state population is $\sim 55\%$ of the total population N_{total} . [9]

$$T = \exp[-(N_{gr}\sigma_o + N_{ex}\sigma_3)d] \quad (1)$$

Figure 1 (B) (C) and (D) show the in situ Raman spectra taken at various points along the intensity-dependent transmission curve of figure 1(A). The dashed lines in the spectra are Lorentzian/ Gaussian fits to the various components. Figure 1(B) shows the low irradiance spectrum ($>10^4 \text{Wcm}^{-2}$) of the pentagonal pinch mode and it is seen to be positioned at 1469cm^{-1} . However at laser powers approaching $\sim 15000 \text{Wcm}^{-2}$ two new components appear in the spectrum figure 1(C). The first component positioned at 1466cm^{-1} has a Raman signature analogous to that reported for the molecular triplet of C_{60} in solution [5]. Indeed one would expect excited state species of C_{60} to have a lower frequency of vibration as they should be in an antibonding state and hence have a weaker intramolecular force of attraction in comparison to the ground state [8]. Van Loosdrecht et al. [8] have reported similar intensity dependent shifting of the A_{2g} pentagonal pinch mode from 1469cm^{-1} to 1459cm^{-1} in C_{60} crystals at low temperatures ($\sim 40\text{K}$). They assigned the observed shifts to electronically excited C_{60} and in particular the triplet state [8]. It should be noted, however, that a population redistribution from ground to triplet state should be characterised by a decrease in the ground state mode and the emergence of a single triplet mode, rather than the quasi-continuous shifting reported by van Loosdrecht et al. Close consideration of the data in question shows an initial discontinuous emergence of a mode at 1466cm^{-1} , which, in comparison to the data presented here and previously for measurements in solution [5] should be assigned to the molecular triplet.

In addition to the feature at 1466cm^{-1} a further reversible shift to 1463cm^{-1} at higher intensities can also be identified both in our data for a thin film and van Loosdrecht's data for single crystals. This feature at 1463cm^{-1} is an excited state species that appears to be specific to the solid state, as similar measurements in solution show no Raman evolution beyond 1466cm^{-1} . This high intensity intermediate state has previously been observed in the depolymerisation of solid C_{60} [1], as well as in reversible processes in C_{60} crystals [10]. This high intensity state has been associated with that which is characterised by a nonlinear photo-luminescence and photo-conductivity [10] and has been speculated to be a co-operative interaction between excited states in the solid, at high excitation densities [10]. That such a state is present, in the depolymerisation of C_{60} may be understood by considering the symmetry conditions of the C_{60} molecules. Initially the molecules have the same symmetry in the ground state. Upon the addition of a single photon

one molecule is promoted to an excited state creating the molecular triplet species as in the proposed 2+2 cycloaddition polymerisation mechanism [6,7]. However as the system has been maintained at 77K the photopolymerisation cannot proceed due to the orientational phase transition. Hence as the intensity is increased a high density of excited states is created in the solid. At high intensities the excited state electronic orbitals of neighbouring molecules can readily overlap and rapidly create an excited state co-operative in which the molecular excited states becomes delocalised across several molecules in the solid creating a species analogous to that observed in the photo-depolymerisation. Finally it should be noted that the pentagonal pinch mode remains ever present but experiences a loss in intensity. The evolution of the three features is evident in figure 1(D) with the feature at 1463cm^{-1} becoming the dominant species at high laser intensities (35000Wcm^{-2}). Upon return to low laser intensities the pentagonal pinch mode once again becomes the dominant species suggesting that the photoinduced processes are fully reversible within the resolution of the instrument. The instantaneous reversibility coupled with the intensity dependence is a strong indication that the new peaks are vibrational modes of excited state C_{60} in the solid.

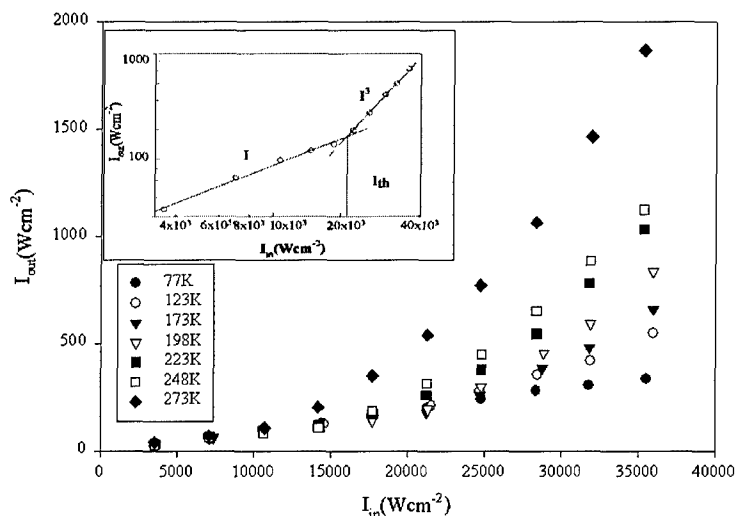


Figure 2. Intensity -Dependent Transmission curves in temperature range 77K-273K. Inset shows cubic fits at 198K.

As the temperature is increased a more non-linear or cubic behaviour emerges and becomes dominant (figure 2). This behaviour is characteristic of non-linearities previously described in crystals [10]. The linear and non-linear components of the intensity dependent transmission curve at 198K are highlighted in the inset figure 2. This non-linear increase in the transmission is indicative of bleaching, in which the excited state absorption cross section is less than the ground state absorption cross section ($\sigma_{ex} < \sigma$). In general at temperatures above the phase transition (249K), the bleaching process can be attributed to the onset of irreversible

photochemical reactions [1,6]. In this case however for temperatures below $\sim 200\text{K}$, there is no evidence of any photochemical reactions occurring, as the in situ Raman spectra as well as the intensity dependent transmission curves are fully reversible, suggesting that the observed changes are purely photophysical. While the intensity dependent transmission curve for 198K is significantly different to the corresponding curve at 77K , the in situ Raman spectra and the evolution of the respective excited states at 1466cm^{-1} and 1463cm^{-1} is comparable to that shown in figure 1 for 77K . A similar temperature dependence for all temperatures below 198K has also been observed.

The change with temperature of the non-linearity can be assessed from the point at which the system deviates from a linear response to a non-linear response in the intensity dependent transmission curves, I_{th} in inset in figure 2. The in situ Raman spectrum of the onset of the non-linearity (i.e. at I_{th}) shows that the co-operative species (at 1463cm^{-1}) is the dominant species at this point for all temperatures, suggesting that this species is non-linear in nature. Such a suggestion supports the notion that this species is analogous to the high intensity state previously reported in single crystals and characterised by a non-linear photoluminescence and photoconductivity [1,10].

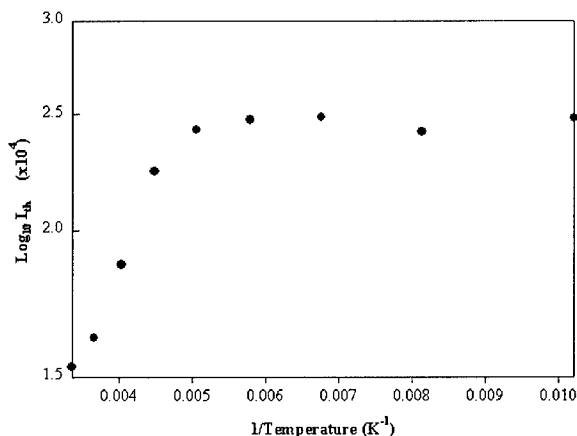


Figure 3. Temperature dependence of cubic response in transmission curves.

A plot of the intensities of the onset of the non-linearity (I_{th}) against the inverse of the temperature shown in figure 3. It can be seen that the non-linearity is independent of temperature up to $\sim 220\text{K}$. This suggests that the electronic delocalisation of the π -electron system, between the molecules in the solid state is intrinsic to the material at temperatures below 220K . It should be noted that this temperature is remarkably close to the orientational phase transition temperature of 249K particularly when one considers the effect of localised laser heating at the point of measurement. The induced Raman shifts observed with intensity are also fully reversible up until 220K however above this temperature the shifts become irreversible. In addition to the irreversibility of the Raman shifts above 220K the temperature independence of the non-linearity rapidly falls to lower intensities suggesting the non-linear delocalised species is formed at much lower intensities. A similar temperature dependence to that shown here was also

observed by Minami et al. for the luminescence spectrum [11] and was suggested to indicate that the decay route in C_{60} films should be regarded as the result of an intermolecular effect such as an intermolecular charge transfer excited state or indeed the high intensity excited state species proposed for the observed changes in our data. Absorption measurements at low temperatures also support the notion that a highly delocalised excited state similar to that proposed for the Raman mode at $\sim 1463\text{cm}^{-1}$ at low temperatures and for the non-linear response observed at high intensity in the transmission curves, is possible [11].

At temperatures beyond 220K the onset of the non-linearity (i.e. I_{th}) is seen to rapidly decrease as shown in figure 3. The bleaching of the system at this temperature unlike the lower temperatures may be attributable to the initiation of irreversible photochemical processes such as the photopolymerisation. In situ Raman spectra confirms that some photochemistry is taking place as the original ground state pentagonal pinch mode is only partially regained upon reduction of the intensity. Nevertheless the data highlights the existence of a highly non-linear delocalised co-operative excited state species at low temperatures which is intrinsic to C_{60} . In addition the Raman signature of the molecular triplet has been identified for the first time in the solid state.

CONCLUSION

A full description of the photophysics of C_{60} after a decade of research has still remained elusive. The data reported here shows clearly the existence of two excited state species in solid thin films of C_{60} , the molecular triplet, positioned at 1466cm^{-1} and an excited state co-operative specific to the solid state positioned at 1463cm^{-1} . The second species has been reported to be intrinsic to C_{60} at low temperatures ($<220\text{K}$).

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